

# Superconductivity in $\text{Yb}_x(\text{Me})_y\text{HfNCl}$ ( $\text{Me} = \text{NH}_3$ and THF)

Guojun Ye, Jianjun Ying, Yajun Yan, Xigang Luo, Peng Cheng, Ziji Xiang, Aifeng Wang, Xianhui Chen\*  
Hefei National Laboratory for Physical Science at Microscale and Department of Physics,  
University of Science and Technology of China, Hefei,  
Anhui 230026, People's Republic of China

The intercalated layered nitride  $\beta\text{-HfNCl}$  has attracted much attention due to the high superconducting transition temperature up to 25.5 K. Electrons can be introduced into  $\beta\text{-MNCl}$  ( $M=\text{Zr}$  and  $\text{Hf}$ ) through alkali-metals intercalation to realize the superconductivity. Here, we report the observation of superconductivity in rare-earth metals cointercalated compounds  $\text{Yb}_x(\text{Me})_y\text{HfNCl}$  with  $\text{Me} = \text{NH}_3$  and tetrahydrofuran (THF), which were synthesized by the liquid ammonia method at room temperature. The superconducting transition temperature is about 23 K and 24.6 K for  $\text{Yb}_{0.2}(\text{NH}_3)_y\text{HfNCl}$  and  $\text{Yb}_{0.3}(\text{NH}_3)_y\text{HfNCl}$ , respectively. Replacing the  $\text{NH}_3$  with a larger molecule THF, superconducting transition temperature increases to 25.2 K in  $\text{Yb}_{0.2}(\text{THF})_y\text{HfNCl}$ , which is almost the same as the highest  $T_c$  reported in the alkali-metals intercalated  $\text{HfNCl}$  superconductors. The  $T_c$  of  $\text{Yb}_{0.2}(\text{THF})_y\text{HfNCl}$  is apparently suppressed by pressure up to 0.5 GPa, while the pressure effect on  $T_c$  becomes very small above 0.5 GPa. The liquid ammonia method is proved to be an effective synthetic method to intercalate metal ions into  $\text{HfNCl}$ . Our results suggest that the superconductivity in these layered intercalated superconductors nearly does not rely on the intercalated metal ions, even magnetic ion.

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High- $T_c$  superconductivity has been observed in layered cuprates and recently discovered iron-based superconductors.<sup>1-3</sup> The proximity to magnetically ordered states for these systems suggested that the magnetic interactions are the crucial force for Cooper pairing in such high- $T_c$  superconductivity, which gives rise to the unconventional nature of the superconductivity in these systems. Superconductivity in other various exotic materials, such as  $\text{Na}_x\text{CoO}_2$ ,  $\text{Sr}_2\text{RuO}_4$  and heavy-fermion systems, was also found to be intimate to magnetism.<sup>4-6</sup> However, for another type of superconducting material of the layered metallonitride halides ( $\text{MNX}$ ,  $M = \text{Ti}$ ,  $\text{Zr}$ ,  $\text{Hf}$ ;  $X = \text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ) with the maximum  $T_c$  as high as 25.5 K,<sup>7</sup> their parent compounds are band insulators and superconductivity seems to have no correlation with magnetism.<sup>8</sup> There exist two types of the layered nitride compounds: one is the ( $\text{FeOCl}$ )-type structure (so called  $\alpha$  structure) with the 2D metal-nitrogen ( $\text{MN}$ ) layer of rectangular lattice; the other is the ( $\text{SmSI}$ )-type one (so called  $\beta$  structure) with the 2D  $\text{MN}$  layer of honeycomb lattice.<sup>9</sup> For the former,  $\text{K}_x\text{TiNCl}$  was reported to display superconductivity with  $T_c = 16$  K.<sup>10</sup> For the latter, usually with  $M = \text{Hf}$ ,  $\text{Zr}$  and  $X = \text{Cl}$ , maximum of  $T_c = 25.5$  K has been achieved in  $\text{Li}_x(\text{THF})_y\text{HfNCl}$ .<sup>7</sup> The parent compounds of the latter, so-called  $\beta\text{-MNCl}$ , consist of alternative stacking of honeycomb  $\text{MN}$  bilayer sandwiched by  $\text{Cl}$  bilayer.<sup>11</sup> Superconductivity is usually induced through doping charge carriers by means of alkali-metal intercalation or producing the  $\text{Cl}$  deficiency.<sup>12,13</sup> Unlike the large pressure effect

on  $T_c$  observed in cuprates or iron-based superconductors, the  $T_c$  in this type of superconductors decreases slightly as the pressure increases<sup>14,15</sup>. However, for cointercalated  $\beta\text{-ZrNCl}$  and  $\beta\text{-HfNCl}$ , the interlayer spacing would strongly affects the superconducting transition temperature. Increase of the basal spacing would lead to the reduction of the tiny warping along the  $K_z$  direction, thus to increase the nesting of the Fermi surface<sup>16</sup>. It is assumed that the modification of the Fermi surface would increase the pairing interaction among the electrons, which would enhance  $T_c$  and the maximum  $T_c$  is found when the basal spacing increased to approximate 15 Å in this type of materials<sup>17</sup>.

In two dimensional superconductors, the spin fluctuation may lead to unconventional pairing and high- $T_c$  superconductivity might emerge<sup>18,19</sup>. Nuclear magnetic resonance (NMR)<sup>20</sup> and muon spin relaxation ( $\mu\text{SR}$ ) experiments<sup>21,22</sup> revealed the two-dimensional nature of superconductivity in this intercalated layered nitride  $\text{MNCl}$ . The  $\text{MN}$  bilayer honeycomb structure is thought to play a main role for the happening of superconductivity.<sup>8</sup> The NMR knight shift suggested a spin-singlet pairing,<sup>23</sup> and tunneling spectroscopy<sup>24,25</sup> as well as specific heat<sup>26</sup> revealed a fully open s-wave-like gap. The tunneling-current measurements<sup>27,28</sup> and specific-heat<sup>31</sup> gave a quite large superconducting gap with the ratio  $2\Delta/k_B T \approx 4.6\text{-}5.2$  or even larger, suggesting the strong coupling superconductivity. However, some recent results, such as the anisotropic gap in large doping level inferred by  $\mu\text{SR}$ <sup>29</sup> and the absence of coherence peak in spin-lattice-relaxation rate revealed by NMR experiment<sup>30</sup>, suggested the unconventional pairing mechanisms. Moreover, relatively high  $T_c$  with extremely low density of states at Fermi level<sup>26,31,32</sup>,

\*Corresponding author; Electronic address: chenxh@ustc.edu.cn

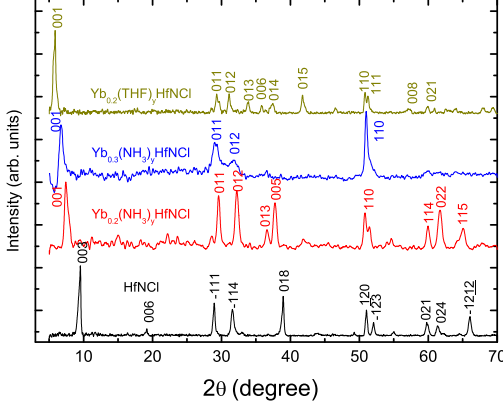


FIG. 1: The x-ray diffraction patterns of pristine  $\beta$ -HfNCI and the superconducting samples of  $\text{Yb}_{0.2}(\text{NH}_3)_y\text{HfNCI}$ ,  $\text{Yb}_{0.3}(\text{NH}_3)_y\text{HfNCI}$  and  $\text{Yb}_{0.2}(\text{THF})_y\text{HfNCI}$ , respectively.

weak electron-phonon coupling<sup>23,31–33</sup> and small isotope effect<sup>34,35</sup> also favor the unconventional pairing mechanisms in these intercalated  $\beta$ -MNCI superconductors. The mystery of the superconductivity for the intercalated  $\beta$ -MNCI compounds is still in debt.

In this report, we reported the discovery of superconductivity by cointercalating magnetic rare earth ion of ytterbium with  $\text{NH}_3$  or THF molecule in HfNCI. Ytterbium was cointercalated with  $\text{NH}_3$  between HfNCI layers by the liquid ammonia method at room temperature, instead of previous methods by reacting in alkali-organic salt/organic solution,<sup>7</sup> electrochemical intercalation,<sup>36</sup> using solid-state reaction with  $\text{K}_3\text{N}$ <sup>37</sup>. Superconductivity with  $T_c$  of  $\sim 23$  K or  $\sim 24.6$  K is discovered in  $\text{Yb}_x(\text{NH}_3)_y\text{HfNCI}$  depending on the Yb content. THF molecule can be also cointercalated with Ytterbium into HfNCI, and the superconductivity with  $T_c$  as high as 25.2 K was observed from magnetic susceptibility, which is nearly the same as the reported maximum  $T_c$  in the alkali-metal intercalated HfNCI compounds. The pressure effect of this sample is negative,  $dT_c/dP$  is about -0.6 GPa/K below 0.5 GPa and it becomes -0.16 GPa/K above 0.5 GPa.

Figure 1 shows the X-ray diffraction (XRD) patterns of  $\beta$ -HfNCI,  $\text{Yb}_{0.2}(\text{NH}_3)_y\text{HfNCI}$ ,  $\text{Yb}_{0.3}(\text{NH}_3)_y\text{HfNCI}$  and  $\text{Yb}_{0.2}(\text{THF})_y\text{HfNCI}$  using Cu  $K_\alpha$  radiations. The XRD pattern of pristine  $\beta$ -HfNCI can be well indexed based on the space group  $R\bar{3}m$ , and the lattice parameters are determined to be  $a=3.58$  Å and  $c=27.71$  Å, being consistent with the previous report<sup>7</sup>. In comparison with that of the pristine  $\beta$ -HfNCI, the XRD patterns of  $\text{Yb}_{0.2}(\text{NH}_3)_y\text{HfNCI}$ ,  $\text{Yb}_{0.3}(\text{NH}_3)_y\text{HfNCI}$  and  $\text{Yb}_{0.2}(\text{THF})_y\text{HfNCI}$  can be indexed based on the space group  $P\bar{3}m$ . The lattice parameters are determined to be  $a=3.59$  Å and  $c=11.95$  Å for  $\text{Yb}_{0.2}(\text{NH}_3)_y\text{HfNCI}$ , and

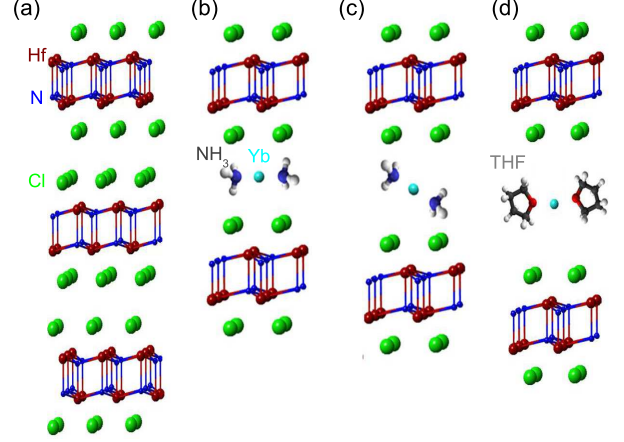


FIG. 2: The schematic structural models for (a): the pristine HfNCI; (b):  $\text{Yb}_{0.2}(\text{NH}_3)_y\text{HfNCI}$ ; (c):  $\text{Yb}_{0.3}(\text{NH}_3)_y\text{HfNCI}$  and (d):  $\text{Yb}_{0.2}(\text{THF})_y\text{HfNCI}$ , respectively.

$a=3.59$  Å and  $c=13.20$  Å for  $\text{Yb}_{0.3}(\text{NH}_3)_y\text{HfNCI}$ , respectively. The lattice parameters change to be  $a=3.59$  Å and  $c=15.05$  Å for  $\text{Yb}_{0.2}(\text{THF})_y\text{HfNCI}$ . The lattice parameters in the  $ab$  plane are almost unchanged for all the intercalated samples, but the stacking pattern of the layers is changed so much, leading to the change in the space group from  $R\bar{3}m$  to  $P\bar{3}m$ . The d-spacing between HfNCI layers increases from 9.24 Å for pristine  $\beta$ -HfNCI to 11.95 Å and 13.20 Å for the superconducting  $\text{Yb}_{0.2}(\text{NH}_3)_y\text{HfNCI}$  and  $\text{Yb}_{0.3}(\text{NH}_3)_y\text{HfNCI}$ , and to 15.05 Å for superconducting  $\text{Yb}_{0.2}(\text{THF})_y\text{HfNCI}$ , respectively. The interlayer spacing  $d$  between MNCI ( $M=\text{Zr}$  or  $\text{Hf}$ ) layers is strongly dependent on the amounts and types of metal ions, and the cointercalated solvent molecules in intercalated MNCI superconductors. The  $c$ -axis lattice parameter of  $c=11.95$  Å for  $\text{Yb}_{0.2}(\text{NH}_3)_y\text{HfNCI}$  is nearly the same as  $c=12.1$  Å of  $\text{Li}_{0.37}(\text{NH}_3)_y\text{HfNCI}$ <sup>16</sup>. It indicates that the stacking structure for  $\text{NH}_3$  cointercalated HfNCI with Yb should be similar to that of  $\text{Li}_{0.37}(\text{NH}_3)_y\text{HfNCI}$ . While for  $\text{Yb}_{0.3}(\text{NH}_3)_y\text{HfNCI}$ , the  $d$ -spacing increases to 13.20 Å, which is possibly due to the different Yb amount and orientation of  $\text{NH}_3$ . The spacing between MNCI ( $M=\text{Zr}$  or  $\text{Hf}$ ) layers increases to 14.9 or 18.5 Å for  $\text{Li}_x(\text{THF})_y\text{ZrNCI}$ ,<sup>38</sup> while to 13.6 or 18.7 Å<sup>16</sup> for  $\text{Li}_x(\text{THF})_y\text{HfNCI}$ . The different spacing between MNCI layers strongly depends on the amounts of lithium and orientation of THF. The  $c$ -axis parameter increases to 15.05 Å for the  $\text{Yb}_{0.2}(\text{THF})_y\text{HfNCI}$ , which is very close to 14.9 Å for  $\text{Li}_x(\text{THF})_y\text{ZrNCI}$ . It suggests that the stacking structure of the  $\text{Yb}_{0.2}(\text{THF})_y\text{HfNCI}$  is the same as that the  $\text{Li}_x(\text{THF})_y\text{ZrNCI}$ . The Schematic structural models for the pristine HfNCI,  $\text{Yb}_{0.2}(\text{NH}_3)_y\text{HfNCI}$ ,  $\text{Yb}_{0.3}(\text{NH}_3)_y\text{HfNCI}$  and  $\text{Yb}_{0.2}(\text{THF})_y\text{HfNCI}$  are pro-

TABLE I: Lattice parameters and  $T_c$  of  $\text{Yb}_x(\text{Me})_y\text{HfNCI}$  ( $\text{Me} = \text{NH}_3$  and THF).

	$\beta\text{-HfNCI}$	$\text{Yb}_{0.2}(\text{NH}_3)_y\text{HfNCI}$	$\text{Yb}_{0.3}(\text{NH}_3)_y\text{HfNCI}$	$\text{Yb}_{0.2}(\text{THF})_y\text{HfNCI}$
space group	$\text{R}\bar{3}\text{m}$	$\text{P}\bar{3}\text{m}$	$\text{P}\bar{3}\text{m}$	$\text{P}\bar{3}\text{m}$
a (Å)	3.58	3.59	3.59	3.59
c (Å)	27.71	11.95	13.20	15.05
d-spacing (Å)	9.24	11.95	13.20	15.05
$T_c$ (K)		23	24.6	25.2

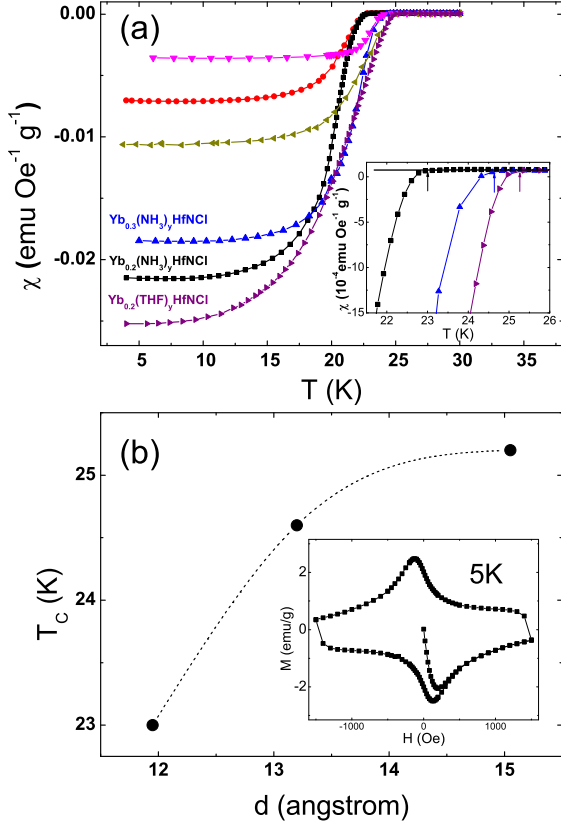


FIG. 3: (a): The ZFC and FC susceptibility taken at 10 Oe for  $\text{Yb}_{0.2}(\text{NH}_3)_y\text{HfNCI}$ ,  $\text{Yb}_{0.3}(\text{NH}_3)_y\text{HfNCI}$  and  $\text{Yb}_{0.2}(\text{THF})_y\text{HfNCI}$ . The inset shows the enlarged area around  $T_c$ . (b): Interlayer spacing  $d$  dependence of  $T_c$  for all the superconducting samples. The inset shows the isothermal magnetization hysteresis of  $\text{Yb}_{0.2}(\text{NH}_3)_y\text{HfNCI}$  taken at 5K.

posed as shown in Fig.2, respectively.

Temperature dependence of zero field cooling (ZFC) and field cooling (FC) magnetic susceptibilities for the superconducting  $\text{Yb}_{0.2}(\text{NH}_3)_y\text{HfNCI}$ ,  $\text{Yb}_{0.3}(\text{NH}_3)_y\text{HfNCI}$  and  $\text{Yb}_{0.2}(\text{THF})_y\text{HfNCI}$  are shown in Fig.3 (a). The zero field cooling (ZFC) susceptibilities shown in the inset of Fig. 3(a) indicate a clear superconduct-

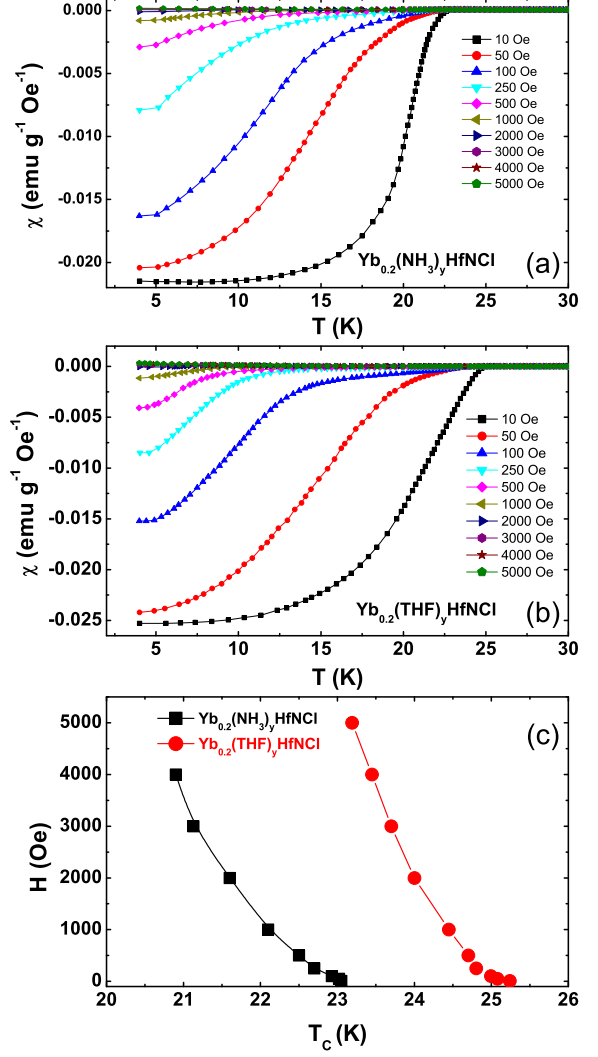


FIG. 4: Temperature dependence of susceptibility for the superconducting samples of (a):  $\text{Yb}_{0.2}(\text{NH}_3)_y\text{HfNCI}$  and (b):  $\text{Yb}_{0.2}(\text{THF})_y\text{HfNCI}$  in the ZFC measurements under different magnetic fields. (c): The  $H_{c2}$  versus  $T_c$  for the samples of  $\text{Yb}_{0.2}(\text{NH}_3)_y\text{HfNCI}$  and  $\text{Yb}_{0.2}(\text{THF})_y\text{HfNCI}$ .

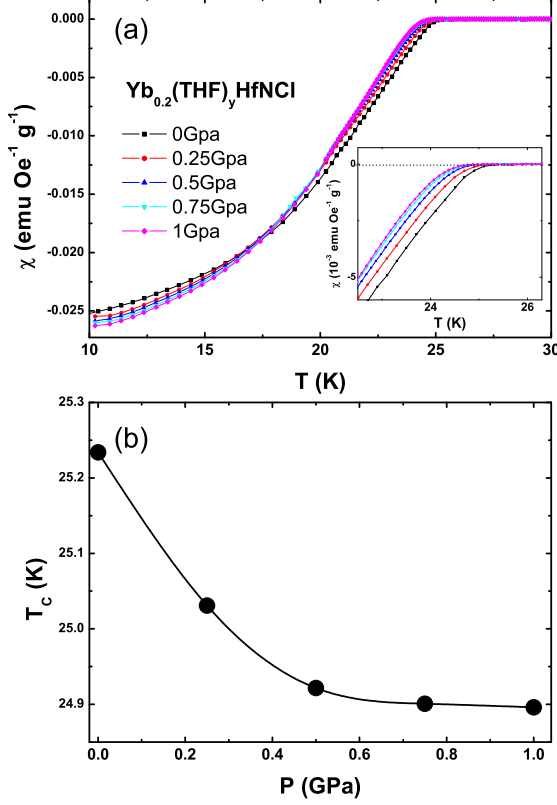


FIG. 5: (a): Temperature dependence of susceptibility for the sample  $\text{Yb}_{0.2}(\text{THF})_y\text{HfNCl}$  in the ZFC measurements under various pressures. The inset is the enlarged area around  $T_c$ . (b): Pressure dependence of  $T_c$  for the sample  $\text{Yb}_{0.2}(\text{THF})_y\text{HfNCl}$ .

ing transition at about 23 K for  $\text{Yb}_{0.2}(\text{NH}_3)_y\text{HfNCl}$ , at 24.6 K for  $\text{Yb}_{0.3}(\text{NH}_3)_y\text{HfNCl}$  and at 25.2 K for  $\text{Yb}_{0.2}(\text{THF})_y\text{HfNCl}$ , respectively. Interlayer spacing  $d$  dependence of  $T_c$  for all the superconducting samples is shown in Fig. 3(b),  $T_c$  slightly increases from 23 K to 25.2 K as interlayer spacing  $d$  increases from 11.95 Å to 15.05 Å. A similar behavior has been observed in  $\text{Li}_x\text{Me}_y\text{HfNCl}$  ( $\text{Me}=\text{NH}_3$  and THF)<sup>16</sup>. The inset of Fig.3(b) shows the isothermal magnetization hysteresis for  $\text{Yb}_{0.2}(\text{NH}_3)_y\text{HfNCl}$  at 5 K. Similar behavior in the M-H is observed for the samples of  $\text{Yb}_{0.3}(\text{NH}_3)_y\text{HfNCl}$  and  $\text{Yb}_{0.2}(\text{THF})_y\text{HfNCl}$ . The lower critical field ( $H_{c1}$ ) for all the superconducting samples are around 80 Oe, which are the same as that of alkali-metal cointercalated  $\text{HfNCl}$ <sup>38</sup>. Lattice parameters and  $T_c$  of  $\text{Yb}_x(\text{Me})_y\text{HfNCl}$  ( $\text{Me} = \text{NH}_3$  and THF) are summarized in Table 1.

Figure 4(a) and (b) show the temperature dependence of the susceptibility in ZFC measurements under various magnetic fields for  $\text{Yb}_{0.2}(\text{NH}_3)_y\text{HfNCl}$  and  $\text{Yb}_{0.2}(\text{THF})_y\text{HfNCl}$ , respectively.  $T_c$  and the diamagnetic signal are gradually suppressed, and the supercon-

ducting transition becomes significantly broad with the application of magnetic fields. Within the weak-coupling BCS theory, the upper critical field  $H_{c2}$  at  $T=0$  K can be determined by the Werthamer-Helfand-Hohenberg (WHH) equation<sup>39</sup>  $H_{c2}(0) = 0.693[-(dH_{c2}/dT)]_{T_c}T_c$ . Using the data of  $H_{c2}(T)$  derived from the susceptibility measurement, one obtains  $[-(dH_{c2}/dT)]_{T_c}$  to be about 0.25 T/K and 0.38 T/K for  $\text{Yb}_{0.2}(\text{NH}_3)_y\text{HfNCl}$  and  $\text{Yb}_{0.2}(\text{THF})_y\text{HfNCl}$ , respectively. Thus, the  $H_{c2}(0)$  can be estimated to be 4 T and 6.6 T for  $\text{Yb}_{0.2}(\text{NH}_3)_y\text{HfNCl}$  and  $\text{Yb}_{0.2}(\text{THF})_y\text{HfNCl}$ , respectively.

Figure 5(a) shows the temperature dependence of the susceptibility in ZFC measurements for  $\text{Yb}_{0.2}(\text{THF})_y\text{HfNCl}$  under various pressures. The inset of Fig. 5(a) shows the enlarged area around  $T_c$ . The  $T_c$  is defined as the temperature at which the susceptibility starts to decrease. The pressure dependence of  $T_c$  was shown in Fig. 5(b).  $T_c$  decreases with increasing the pressure.  $T_c$  decreases at a relative quick speed with  $dT_c/dP=-0.6$  GPa/K below 0.5 GPa. While the pressure effect becomes very small above 0.5 GPa with  $dT_c/dP=-0.16$  GPa/K. Such behavior is similar to the observation in the alkali-metals intercalated  $\text{HfNCl}$  and  $\text{ZrNCl}$ <sup>14,15</sup>.

Electron-doping of  $\beta$ - $\text{HfNCl}$  is usually realized by the intercalation of alkali metals or cointercalation of alkali metals with molecules. Here, we report the superconductivity in electron-doped  $\text{HfNCl}$  by cointercalation of rare-earth magnetic ion with molecules. It is striking that the maximum  $T_c$  of 25.2 K observed in  $\text{Yb}_{0.2}(\text{THF})_y\text{HfNCl}$  is almost the same as the highest  $T_c$  in the alkali metals cointercalation with THF. It indicates that superconductivity in the intercalated  $\text{HfNCl}$  does not rely on the different intercalated ions, even magnetic ion. It is intriguing that the intercalation of magnetic ion of rare-earth metal Yb does not affect the superconductivity relative to the intercalation of alkali-metal ion. It indicates that magnetism does not suppress the superconductivity, being an evidence for unconventional superconductivity. The  $T_c$  increases from 23 K to 25.2 K with increasing the interlayer spacing from 11.95 Å for  $\text{Yb}_{0.2}(\text{NH}_3)_y\text{HfNCl}$  to 15.05 Å for  $\text{Yb}_{0.2}(\text{THF})_y\text{HfNCl}$ . Such slight enhancement of  $T_c$  induced by large increase of the interlayer spacing indicates the good two-dimensional electronic system for the intercalated  $\text{HfNCl}$  superconductors, which could be the reason why superconductivity in the intercalated  $\text{HfNCl}$  does not rely on the intercalated ions. The liquid ammonia method is proved to be a good way to intercalate metal ions into  $\text{MNCl}$  ( $\text{M}=\text{Zr}$  and  $\text{Hf}$ ) to introduce electron in the system and realize superconductivity. An interesting question is whether  $T_c$  could be raised to above 25.5 K in the intercalated  $\text{HfNCl}$  system or not.

**Materials and Methods**  $\beta$ - $\text{HfNCl}$  was synthesized by reacting of Hf powder and gasified  $\text{NH}_4\text{Cl}$  in the environment of ammonia at 923 K for 30 minutes, then the product was sealed in a quartz tube followed by a vapor transport recrystallized process from low tem-

perature side to high temperature side at the temperature gradient of 1023 K to 1123 K with the aid of a small amount of  $\text{NH}_4\text{Cl}$  as transport agent. We can obtain two types of  $\text{Yb}_x(\text{NH}_3)_y\text{HfNCl}$  by adjusting the Yb content. 0.1 gram of recrystallized  $\text{HfNCl}$  together with 0.053 or 0.068 gram of ytterbium, then the mixture were loaded in a 50 ml autoclave which was cooled by liquid nitrogen, the autoclave was slowly filled with 15 ml liquid ammonia and sealed. The sealed autoclave was kept at room temperature for 1-3 days before it was opened and dried in the glove box. The products were rinsed by using liquid ammonia to eliminate soluble impurities, thus we can obtain the final product. The actual Yb concentration (x) of these two samples were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES), and the actual x values are 0.2 and 0.3, respectively.  $\text{Yb}_{0.2}(\text{THF})_y\text{HfNCl}$  can be

synthesized by immersing the  $\text{Yb}_{0.2}(\text{NH}_3)_y\text{HfNCl}$  powder into THF solution for 1-2 days, while we can not obtain  $\text{Yb}_{0.3}(\text{THF})_y\text{HfNCl}$  by the same method. All the experiments were performed under Ar atmosphere to prevent it from air and water contamination. The x-ray diffraction (XRD) was carried out with samples sealed in capillaries that were made of special glass No. 10 and purchased from Hilgenberg GmbH. The magnetization measurement was performed by using SQUID MPMS-5T (Quantum Design). The magnetization under pressure was measured by incorporating a copperCberyllium pressure cell (EasyLab) into SQUID MPMS (Quantum Design). The sample was firstly placed in a teflon cell (EasyLab) with coal oil (EasyLab) as the pressure media. Then, the teflon cell was set in the copper-beryllium pressure cell for magnetization measurement.

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